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AFCI - Corrosion Milestone Report: 2002 WNR Irradiation Experiments

The Influence of Proton Irradiation on the Oxide Film Properties of HT-9 in LBE

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Abstract

The oxide dielectric properties of the martensitic-ferritic steel HT-9 were characterized during proton irradiation at the LANSCE WNR facility. Prior to the irradiation experiment, samples were preoxidized in moist air resulting in an oxide scale that was on the order of 3 μm in thickness. Samples were then irradiated during immersion in 200° C lead-bismuth eutectic at a proton current of approximately 61 nA. To assess electrical properties of the oxide in real-time, a sinusoidal voltage perturbation is applied across the oxide surface as a function of frequency. By measuring the magnitude and phase shift in the current response oxide impedance and capacitance values were obtained. For HT-9, proton irradiation was associated with a decrease in oxide impedance in 2-out-of-3 experiments. This change in oxide electrical properties is consistent with increased corrosion rates during proton irradiation. This decrease in corrosion resistance is most likely due local chemical, structural, or electronic changes in oxide properties though global changes in oxide properties are possible as well. Defects in the oxide that permit direct contact between the LBE and metal surface are ruled out. Although we were prepared to examine the oxide properties of SS 316, time constraints did not permit these experiments.

Introduction

The purpose of these experiments was to determine whether or not there is an influence of proton irradiation on the corrosion properties of structural materials in lead bismuth eutectic (LBE) coolant. In this system, an oxide film provides the material with protection from the LBE. To access oxide properties in real-time, we have used an impedance technique. In this method a sinusoidal voltage perturbation is applied across the oxide surface as a function of frequency. This method yields values for oxide impedance and capacitance. In general, high values for oxide impedance and low values for oxide capacitance are associated with protecting oxide layers.

Experimental

Experiments were conducted at the Weapons Neutron Research facility (WNR) of LANSCE. This facility provided access to the proton beam such that a conventional three electrode electrochemical cell (discussed below) could be used for real-time irradiation experiments. The flux of the incident proton beam had a Gaussian distribution of $\sigma \approx 0.7$ cm. The energy of this particle beam was 800 MeV. The pulsed beam was characterized by a gate length (macropulse) of 100 μs and a macropulse repetition rate of 100 Hz, and a fixed peak current 16 mA (Figure 1). These duty cycle parameters yielded an average proton beam current of 63 nA.

HT-9 samples were prepared by polishing to 4000 p and sequentially cleaning in acetone, ethanol, and DI water. This was followed by oxidation in moist air at 800° C for 48 hrs. Following grinding, cleaning, and preoxidation the samples were subsequently immersed in LBE (no irradiation) for up to 72 hrs.

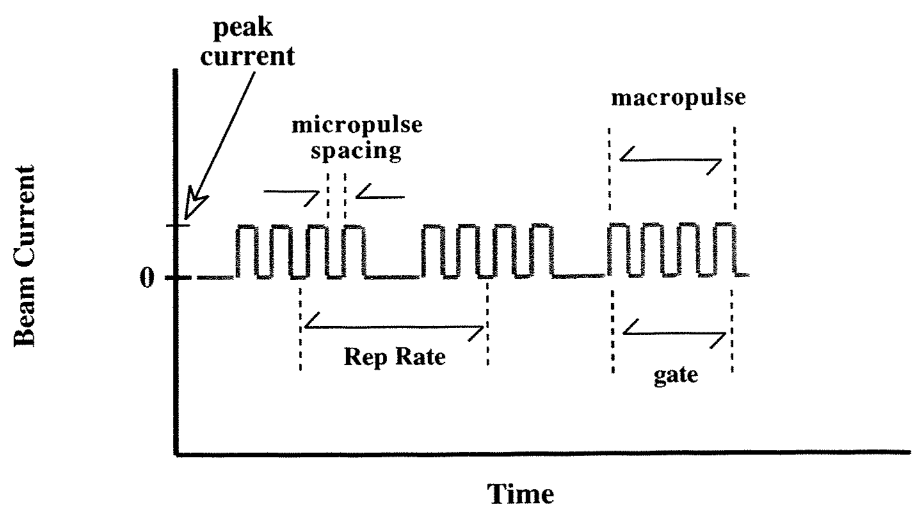


Figure 1 A diagram depicting the proton beam current time relationships and nomenclature.

WNR corrosion experiments were carried out in the furnace depicted in Figure 2. Similar to our laboratory experiments, this furnace was made from off-the-shelf 1.5" o.d. 304L tubing (ultra high vacuum tubing). Heating was supplied by a 700W band heater (1" x 2" diam.) and regulated to within 3° C of the set point with an Omega controller and a type K thermocouple. To avoid excessive oxidation of the LBE melt, the furnace was continuously flushed with Ar during the course of the experiments. A photograph of the actual WNR set-up is shown in Figure 3. To minimize exposure to radiation, as a result of proton activation of the LBE, a lead wall was constructed to separate workers from the furnace. The sample to be tested in this furnace assembly was welded to the end of a piece of SS 304 tubing. At the opposite end the tubing was welded to a kf-type electrical feed through that electrically isolated the sample from the SS furnace (Figure 4).

Impedance data were conducted with a 10 mV peak-to-peak sinusoidal voltage perturbation over the frequency range of 0.005 - 1.0×10^5 Hz. No applied dc potential was employed; that is, all measurements were conducted at the open circuit potential (OCP). To eliminate the effects of ground loops, a floating ground EIS system was used. In these measurements, the traditional three electrode set-up was employed. Because a traditional metal oxide reference was not suitable for the present configuration, a piece of SS 304L tubing was used as a reference.

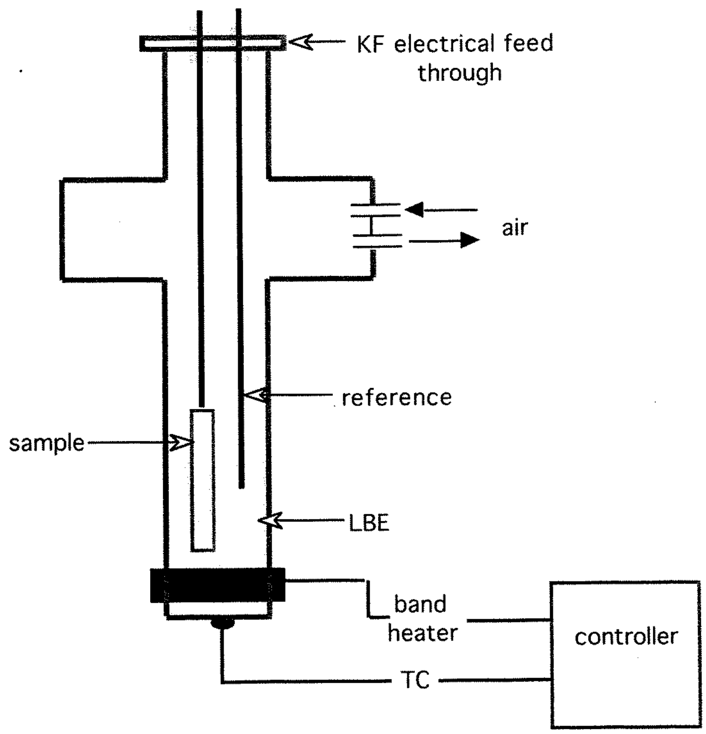


Figure 2 A diagram of the LBE furnace used for oxide dielectric measurements.

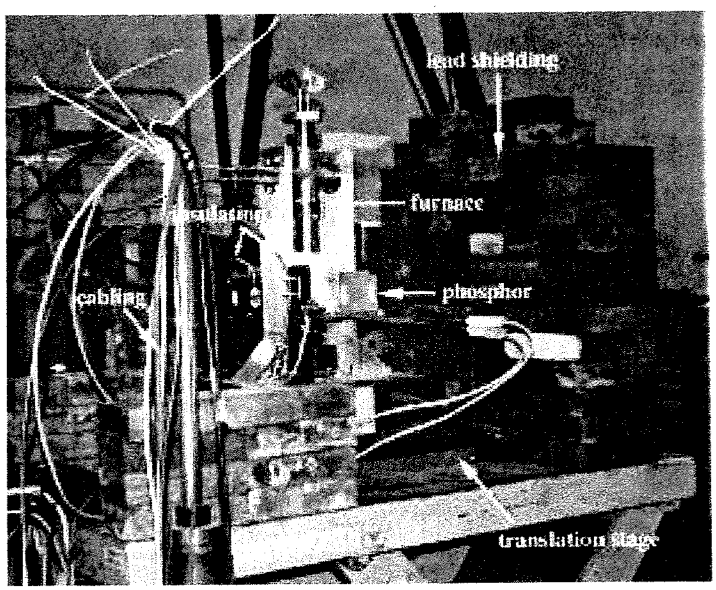
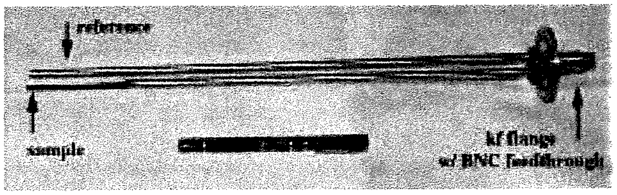


Figure 3 Photograph of the furnace at WNR used for in-beam experiments.



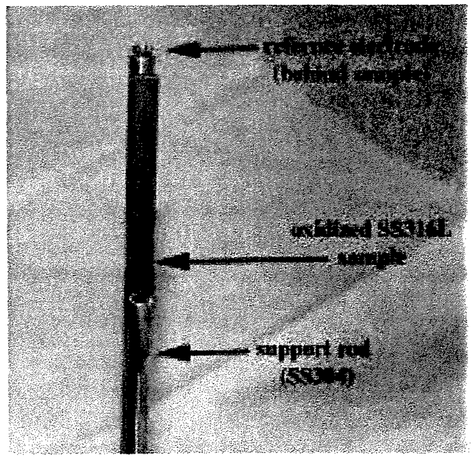


Figure 4 Photographs of the feed through (left), sample, and reference electrodes (right).

Results and Discussion

Typical Bode magnitude and phase data from HT-9 after 24 hrs. of immersion in LBE are presented in Figure 5 (not irradiated). The sample was preoxidized at 800° C for 48 hrs. in moist air prior to immersion. The data are typical of an RC circuit with a high time constant as anticipated for thin semiconducting oxide films (Figure 6). Although the data may appear incomplete, C_{ox} and R_{ox} are readily obtainable from these data using a complex non-linear least squares fitting routine (CNLS). For this report, we will use the value of oxide impedance at 1 kHz as an indicator of oxide properties.

The influence of proton irradiation on HT-9 oxide impedance is shown in Figure 7. Prior to irradiation oxide impedance was monitored for approximately 230 minutes. During this period a logarithmic increase in impedance was observed with immersion time. After 220 min. the impedance appeared to be reaching a plateau on the order of 10^4 ohm·cm^2. Upon turning the beam on to a value of 63 nA after approximately 240 min. of immersion in LBE a sharp fall in impedance was observed. This decline in impedance continued throughout the 30 min. irradiation period. After turning the beam off, oxide impedance was monitored for an additional

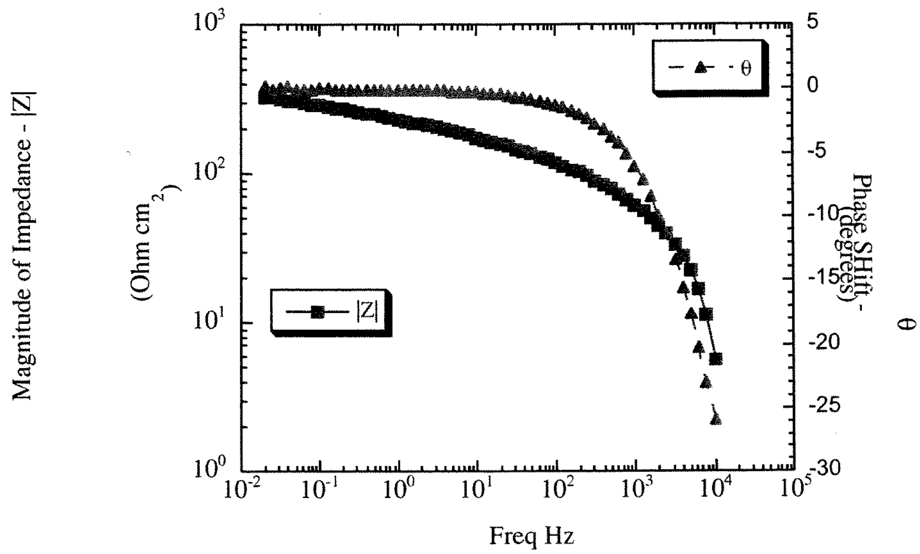


Figure 5 Bode magnitude and phase data from a preoxidized (48 hrs. @ 800° C) HT-9 sample after 24 hrs. of immersion in LBE.

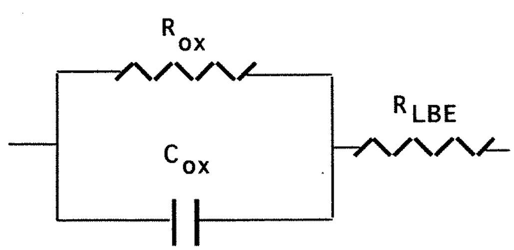


Figure 6 Electrical equivalent circuit representing the oxide / LBE interface.

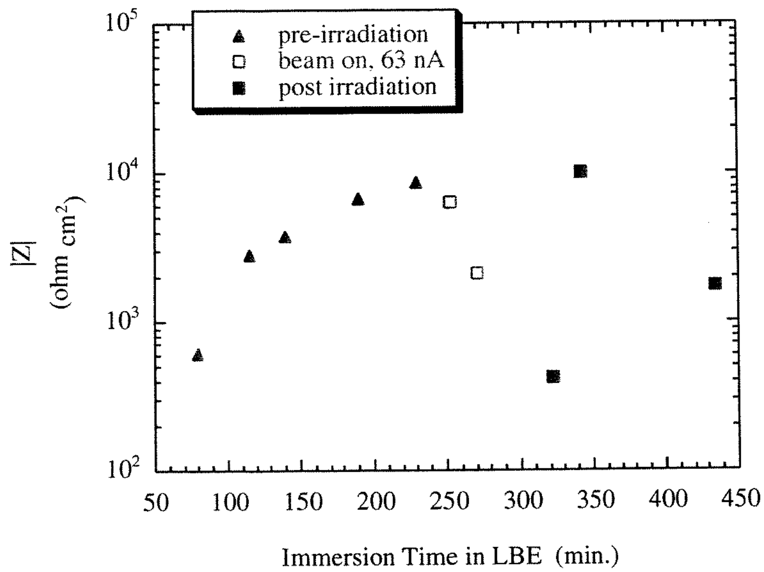


Figure 7 Oxide impedance as a function of LBE immersion time for a preoxidized HT-9 sample (48 hrs. @800° C). Plot shows pre-irradiation, irradiation and post-irradiation data.

640 min.(not all data shown). This period was characterized by widely fluctuating oxide impedance values. This type of behavior was not observed in un-irradiated samples and indicates an inability of the sample to repassivate.

The behavior observed in Figure 7 was not always observed for preoxidized HT-9 samples. In a separate HT-9 experiment, a preoxidized sample with a higher initial impedance value maintained passivity during its initial exposure to the proton beam. The data are shown in Figure 8. Although this sample of HT-9 was preoxidized in the same batch run as the sample in Figure 7 (48 hrs. @ 800° C), it had a higher initial value of oxide impedance which remained constant throughout the pre-irradiation period. Upon turning the beam on to 61 nA at approximetly 160 min, no change in oxide impedance was observed. The post-irradiation period was characterized by stable, impedances that did not differ from the pre-irradiation values. It is concluded that irradiation does not always result in failure of the dielectric properties of the film. Further, it is possible that initial values of the oxide impedance are an indicator of irradiation properties. As seen in Figure 8, after removal of the sample from the LBE bath and re-immersion the oxide

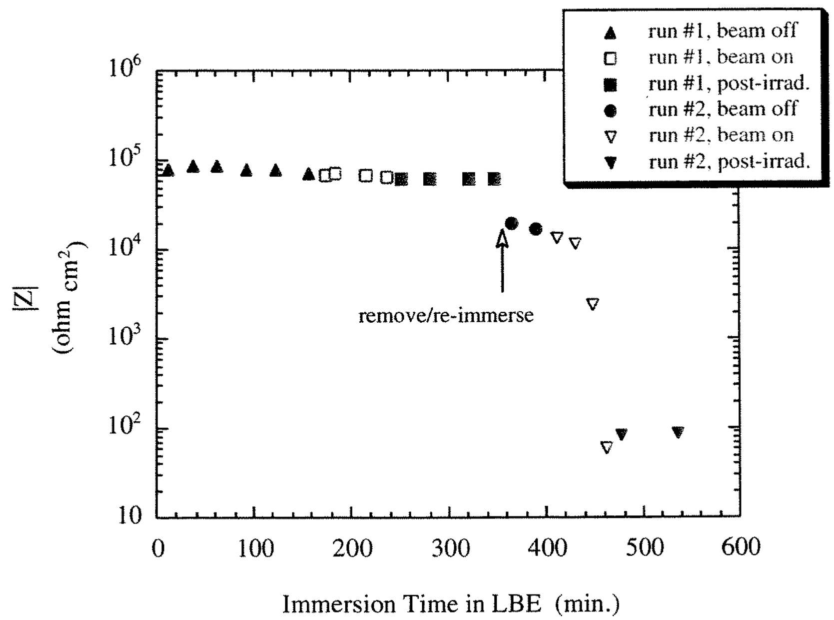


Figure 8 Oxide impedance at 1.0 kHz as a function of immersion time in LBE. After approximately 360 min. of immersion the sample was removed from the LBE furnace for several hours. The sample was then re-introduced into the furnace and measurements were continued.

impedance fell from approximately 6 x10^4 $\Omega{\cdot}cm^2$ to 1.8 x10^4 $\Omega{\cdot}cm^2$. This value was closer to the steady state value of impedance observed in the sample that failed during irradiation in Figure 7. Upon turning the beam on to a current of 61 nA at approximately 400 min. a sharp decrease in oxide impedance was observed (Figure 8). After turning the beam off, the impedance values remained low indicating that the irradiation induced changes in dielectric properties were irreversible. Similar observations were made for the sample tested in Figure 7.

The observed decrease in oxide impedance during proton irradiation may be explained by local or global changes in oxide film properties. Global changes seem unlikely as one might predict consistent/reproducible behavior if the average response of the oxide were controlling. Local changes such as structural, electrical, or chemical changes in the oxide seem more feasible. Electrical changes include metallization of the oxide film that may owe to Cr(III) dissolution into the melt. A pinhole that allows LBE to come in direct contact with the metal substrate is ruled out. The contact impedance for bare metal in LBE (as measured by scratching) is on the order of 0.3 Ω. This impedance acts in parallel with the oxide impedance. Thus, if a pinhole were present, one might anticipate measured impedances less than 0.3 Ω. For our 5 cm^2 sample the minimum measured impedance was on the order of 20 Ω (65 - 320 $\Omega \cdot cm^2$). In addition, the geometric impedance associated with such a defect can not account for these relatively high values. The geometric impedance of the defect (R_Ω) is equal to:

$$R_\Omega = \frac{\rho L}{A}$$

where ρ is resistivity of the LBE, L is the oxide thickness and A is the area of the pinhole. For ρ(Pb-Bi)= 80 $\times 10^{-6}$Ωcm, L=3$\times 10^{-3}$ cm, and A= 3$\times 10^{-6}$ cm^2 one calculates R_Ω=0.08Ω. Thus, local chemical, structural, or electronic changes provide a more plausible explanation for the observed decrease in oxide impedance during irradiation. Although time restraints did not permit further investigation of this phenomena, we are pursuing other methods for reproducing and characterizing this phenomena in out-of-beam experiments. In these experiments preoxidized samples will be irradiated using an ion beam (such as carbon) to produce an equivalent neutron/proton damage. These samples will then be examined in the lab using impedance, TEM and TGA methods.

Summary

- The oxide dielectric properties of the martensitic-ferritic steel HT-9 were characterized during proton irradiation at the LANSCE WNR facility.
- Samples were preoxidized in moist air at 200° C prior to the irradiation.
- During irradiation, samples immersed in LBE and the real-time oxide dielectric properties were measured.
- In 2 out of 3 irradiation experiments a decrease in oxide impedance was observed.
- The observed changes in oxide impedance during irradiation were attributed to local changes in chemical, structural, or electronic properties of the oxide. Unfortunately, time restraints did not permit further investigation of this phenomena.

❖ It is anticipated that future TEM characterization of ion beam irradiated samples will help explain the observed decrease in oxide impedance during the WNR irradiation.